

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-240149

(43)Date of publication of application : 30.08.1994

(51)Int.Cl.

C08L101/00  
C08K 7/04  
// H05B 6/76  
(C08L101/00  
C08L 23:26  
C08L 67:04 )

(21)Application number : 05-030522

(71)Applicant : TEIJIN CHEM LTD

(22)Date of filing : 19.02.1993

(72)Inventor : TAKAGI MAKOTO

## (54) RESIN COMPOSITION FOR SHIELDING ELECTROMAGNETIC WAVE

## (57)Abstract:

PURPOSE: To obtain a resin composition for shielding electromagnetic wave having splendidly shielding effect on electromagnetic wave, excellent mechanical characteristics, molding fluidity and surface appearance.

CONSTITUTION: A thermoplastic resin composition containing electrically- conductive fibers is mixed with (A) at least one compound selected from an olefinic wax and an olefinic polymer containing a carboxylic acid anhydride group and/or a carboxyl group and (B) a polycaprolactone having  $\leq 40,000$  number-average molecular weight to give the objective resin composition for shielding electromagnetic wave.

## LEGAL STATUS

[Date of request for examination]

06.06.1996

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

2819506

[Date of registration]

28.08.1998

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] at least a kind of compound 0.05 chosen as the thermoplastics constituent 100 weight section containing conductive fiber from the olefin system wax and olefin system polymer which have (A) carboxylic anhydride group and/or a carboxyl group -- 30 weight sections -- and -- Resin constituent for electromagnetic wave electric shielding which comes to blend the with a (B) number average molecular weight of 40,000 or less poly caprolactone 1 -- 10 weight sections.

---

[Translation done.]

**\* NOTICES \***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

**[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the suitable resin constituent for electromagnetic wave electric shielding. Furthermore, it is related with the resin constituent for electromagnetic wave electric shielding which has the electromagnetic wave shielding effect which was excellent in a small amount of conductive fiber in detail, and was excellent in a mechanical property especially shock resistance, the shaping fluidity, and the surface appearance.

**[0002]**

**[Description of the Prior Art]** As an approach of electric-conduction-izing thermoplastics, there are an approach by surface preparation, such as conductive coating material, electromagnetic wave electric shielding plating, and zinc spraying, the approach of blending and fabricating conductive fillers, such as a metal powder, carbon black, a metal flake, a metal coat glass flake, a metal fiber, a carbon fiber, and a metal coat carbon fiber, in thermoplastics, etc. However, the approach by surface treatment needs the complicated processing process which carries out electric conduction processing for the fabricated case mold-goods front face, and it has the fault of a conductive layer tending [ further ] to exfoliate.

**[0003]** Moreover, the approach of fabricating from the resin constituent which blended the conductive filler does not need special post processing, but from there being no fear of a conductive layer exfoliating, although it is advantageous, there are still in addition various problems. For example, the resin constituent which blended particle-like conductivity fillers, such as carbon black, a metal powder, and a metal flake, has inadequate conductivity, and since loadings moreover become abundant, the mechanical property has the fault which falls remarkably. Although conductivity is good and useful as a resin constituent for electromagnetic wave electric shielding as compared with that the resin constituent which blended fibrous conductivity fillers, such as copper fiber, stainless steel fiber, a carbon fiber, and a metal coat carbon fiber, again is mechanical, and the case where the thermal property improved and a particle-like conductivity filler is blended, It is easy to cut fiber at the time of melting kneading, loadings must be made [ many ] more than an initial complement, and there is a fault of becoming aggravation of fabricating-operation nature and a mold-goods appearance, buildup of specific gravity, and cost high. For this reason, the appearance of the resin constituent for electromagnetic wave electric shielding which has the electromagnetic wave shielding effect excellent in a small amount of conductive fiber, and was excellent in the mechanical property, the shaping fluidity, and the surface appearance is demanded.

**[0004]**

**[Problem(s) to be Solved by the Invention]** This invention aims at offering the resin constituent for electromagnetic wave electric shielding which has the outstanding electromagnetic wave shielding effect, and was excellent in the mechanical property, the shaping fluidity, and the surface appearance. As a result of repeating examination wholeheartedly that the above-mentioned object should be attained, this invention persons reached [ that the resin constituent for electromagnetic wave electric shielding which suits the thermoplastics constituent containing

conductive fiber at the above-mentioned object when the amount addition of specification of the poly caprolactone which has the olefin system wax and olefin system polymer which have a carboxyl group, and specific number average molecular weight is carried out is obtained, and ] this invention, as a result of repeating examination further, a header and.

[0005]

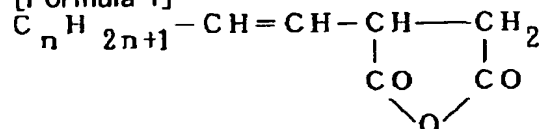
[Means for Solving the Problem] the thermoplastics constituent 100 weight section in which this invention contains conductive fiber, at least a kind of compound 0.05 chosen from the olefin system wax and olefin system polymer which have (A) carboxylic anhydride group and/or a carboxyl group - 30 weight sections -- and -- The resin constituent for electromagnetic wave electric shielding which comes to blend the with a (B) number average molecular weight of 40,000 or less poly caprolactone 1 - 10 weight sections is started.

[0006] The thermoplastics used by this invention is not limited fundamentally, and the thermoplastics used especially for the case of electronic equipment is used preferably. As this thermoplastics, polypropylene resin, styrene resin, modified polyphenylene oxide resin, polyamide resin, polycarbonate resin, polyphenylene sulfide resin, polyester system resin, etc. are raised, for example, as an especially desirable thing -- for example, -- ABS plastics, polycarbonate resin, polyethylene terephthalate resin, polybutyrene terephthalate resin, and two or more sorts of such mixture are raised.

[0007] It is not necessary to restrict especially the conductive fiber used by this invention for example, metal fibers, such as stainless steel fiber, aluminum fiber, copper fiber, and brass fiber, a carbon fiber, a metal coat carbon fiber, a metal coat glass fiber, etc. are raised, and two or more sorts of these can also be used together. Stainless steel fiber, copper fiber, and a metal coat carbon fiber are raised as that from which the conductive resin constituent which was excellent in the electromagnetic wave shielding effect especially is obtained. As a metal fiber, a diameter is 6-80 micrometers. A thing is desirable and it is 6-60 micrometers. Especially a thing is desirable. As a carbon fiber, a metal coat carbon fiber, and a metal coat glass fiber, a diameter is 6-20 micrometers. Especially a thing is desirable. As for this conductive fiber, what carried out surface treatment by the silane coupling agent, the titanate coupling agent, the aluminates coupling agent, etc. is desirable. Moreover, what carried out focusing processing by olefin system resin, styrene resin, polyester system resin, epoxy system resin, urethane system resin, etc. is desirable. What carried out focusing processing by epoxy system resin or urethane system resin especially is desirable. since the conductivity as a resin constituent for electromagnetic wave electric shielding will become inadequate if there is too little amount of the conductive fiber used, and shaping will become difficult if it is made [ many / too much ] -- the total quantity of thermoplastics and conductive fiber -- receiving -- usually -- 0.5 to 30 capacity % -- it is one to 25 capacity % preferably.

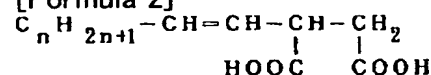
[0008] The olefin system wax and olefin system polymer which have the carboxylic anhydride group and/or carboxyl group who use it by this invention (it will call for short if it only has a carboxyl group below) are the wax or polymer obtained by carrying out acid treatment of an olefin system wax or the olefin system polymer. As a desirable example of the olefin system wax which has a carboxyl group, it is the following type. [0009]

[Formula 1]



[0010]

[Formula 2]

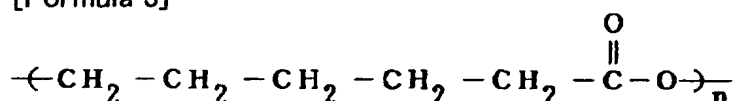


[0011] [-- n is the integer of 12-20 among a formula.] \*\* is raised. Using together two or more sorts of the olefin system waxes and olefin system polymers which have a carboxyl group, the

amount used is 0.05 – 30 weight section to a total of 100 weight sections of thermoplastics and conductive fiber. If there is less this amount used than the 0.05 weight section, even if an electromagnetic wave shielding effect and the shock-proof improvement effectiveness will use it small more mostly than 30 weight sections, since it does not improve any more but a moldability comes to fall to reverse, an electromagnetic wave shielding effect and an impact resistance value are not suitable.

[0012] The poly caprolactone used by this invention is the polymer of a caprolactone, and is especially, the ring-opening-polymerization object, i.e., following general formula, of epsilon-caprolactone. [0013]

[Formula 3]



[0014] It comes out and the polymer shown is desirable. A part or all of a methylene chain of a hydrogen atom may be permuted by the halogen atom, the hydrocarbon group, etc., and end processing of the end may be carried out according to esterification etc. [ of the poly caprolactone ] The poly caprolactone usually has the number average molecular weight of 5,000–300,000, the melting point is about 60 degrees C, and glass transition temperature is [ about ]. – It is 60 degrees C. In this invention, number average molecular weight uses 40,000 or less poly caprolactone. In having used the poly caprolactone with larger number average molecular weight than 40,000, the appearance of mold goods is fully hard to be improved. The catalyst of an acid, a base, an organometallic compound, etc. can carry out bottom ring opening polymerization of existence of the caprolactone, and this poly caprolactone can manufacture it.

[0015] the amount of the poly caprolactone used — a total of 100 weight sections of thermoplastics and conductive fiber — receiving — 1 – 10 weight section — it is 1 – 7 weight section preferably. If there are few amounts of the poly caprolactone than 1 weight section, it will fully be hard to improve an electromagnetic wave shielding effect, a shaping fluidity, and a mold-goods appearance, and if it increases more than 10 weight sections, shaping not only becomes difficult, but a mechanical strength and a thermal property will come to deteriorate.

[0016] In order to manufacture the resin constituent of this invention, the approach and equipment of arbitration can be used. The above-mentioned need component For example, the extruder of a monopodium or two shafts, a Banbury mixer, How to mix with a heating roller etc. and fabricate with the approach of pelletizing, an injection molding machine, etc. directly, Moreover, the approach of mixing the remaining components, after mixing two components of arbitration, or three components beforehand, For example, the approach of mixing the poly caprolactone with the olefin system wax and olefin system polymer which have a carboxyl group after mixing thermoplastics with conductive fiber first, The approach of adding conductive fiber on the pellet which consists of thermoplastics, the olefin system wax and olefin system polymer which have a carboxyl group, and a poly caprolactone, the so-called masterbatch method which adds the master which carried out focusing processing of the conductive fiber at high concentration are held.

[0017] the resin constituent of this invention — the additive of arbitration, for example, a flame retarder, a fire-resistant assistant, a drip inhibitor, a thermostabilizer, an antioxidant, light stabilizer, a release agent, a plasticizer, a coloring agent, lubricant, a foaming agent, etc. — the need — responding — the — even if it carries out the amount combination of effective manifestations, it does not interfere. Furthermore, other reinforcement, such as a conductive filler, for example, carbon black, a metal powder, and a metal flake, and a filler, for example, a glass fiber, a glass flake, a whisker, an aramid fiber, talc, a mica, straw SUTONAITO, clay, a silica, glass powder, a calcium carbonate, etc. can also be used together. Moreover, other thermoplastics, elastic bodies, etc. may be blended.

[0018]

[Example] An example is raised to below and this invention is further explained to it. In addition, assessment was performed by the following approach.

(a) Electromagnetic wave shielding effect : use one-side 150mm and a test piece with a thickness of 3mm, and it is the ADVANTEST CORP. make. TR-17301A R3361A It used together and measured about the field wave (frequency of 300MHz).

(b) Impact strength: It measured by ASTM D-256 (the Izod notch, thickness of 3.2mm).

(c) Shaping fluidity : the Archimedes mold spiral flow value (depth: 8mm, passage thickness:1mm, and injection-pressure 1200 kgf/cm<sup>2</sup>) estimated.

(c) Mold-goods appearance : one-side 150mm and a test piece with a thickness of 3mm were observed visually, \*\* estimated x and a little many things, and O estimated the smooth thing for what has many floats of conductive fiber.

[0019]

[Examples 1-7 and the examples 1-12 of a comparison] 1 shaft extruder [ with the vent of 30mm of diameters of the screw after carrying out dryblend at a rate which shows the olefin system wax or polymer, and the poly caprolactone which have polycarbonate resin, conductive fiber, and a carboxyl group in a table 1 ] [— :VSK-30made from NAKATANI Machine] They are the cylinder temperature of 290 degrees C, the die temperature of 80 degrees C, and injection-pressure 1200 kgf/cm<sup>2</sup> by the injection molding machine [:( by the Japan Steel Works, Ltd. ) J-120 SA] after carrying out melting kneading at 290 degrees C of cylinder temperatures, obtaining a pellet by strand cut and drying the obtained pellet with a hot blast circulation type dryer at 110 degrees C for 5 hours. Spiral flow length was measured and the electromagnetic wave electric shielding test piece, the test piece for appearance assessment, and the impact test specimen were obtained further. The assessment result was shown in a table 1.

[0020]

[Examples 8 and 9 and the examples 13 and 14 of a comparison] ABS 1 shaft extruder [ with the vent of 30mm of diameters of the screw after carrying out dryblend at a rate which shows the olefin system wax or polymer, and the poly caprolactone which have resin, polybutyrene terephthalate resin, conductive fiber, and a carboxyl group in a table 2 ] [— :VSK-30made from NAKATANI Machine] After carrying out melting kneading at 240 degrees C of cylinder temperatures, obtaining a pellet by strand cut and drying the obtained pellet with a hot blast circulation type dryer at 80-110 degrees C for 5 hours, they are the cylinder temperature of 240 degrees C, the die temperature of 80 degrees C, and injection-pressure 1200 kgf/cm<sup>2</sup> by the injection molding machine [:( by the Japan Steel Works, Ltd. ) J-120SA]. Spiral flow length was measured and the electromagnetic wave electric shielding test piece, the test piece for appearance assessment, and the impact test specimen were obtained further. The assessment result was shown in a table 2.

[0021] The notation of the olefin system wax which has the resin in tables 1 and 2, conductive fiber, and a carboxyl group or a polymer, and the poly caprolactone is shown below. Moreover, the weight section which capacity % which shows the rate of conductive fiber shows the rate to the sum total capacity of resin and conductive fiber, and shows the rate of the olefin system wax which has a carboxyl group or a polymer, and the poly caprolactone shows the rate to a total of 100 weight sections of resin and conductive fiber.

[0022] PC: Polycarbonate resin [the Teijin Chemicals bread-making light L-1225]

ABS : ABS-plastics [— Mitsui Toatsu Chemicals, Inc. SANTAKKU UT-61]

PBT : polybutyrene terephthalate resin [ TRB-K by Teijin, Ltd.]

NiCF: Nickel coat carbon fiber [BESUFAITO MC HTA-Cby Toho Rayon Co., Ltd. 6-US (I), the diameter of 7.5 micrometers, and die length of 6mm]

CF: Carbon fiber [BESUFAITO [ by Toho Rayon Co., Ltd. ] HTA-C6-U, the diameter of 7 micrometers, and die length of 6mm]

SUS : stainless steel fiber [Naslon [ by Nippon Seisen Co., Ltd. ] SUS304, the diameter of 8 micrometers, and die length of 6mm]

COL An olefin system wax or polymer W-1 which has :carboxyl group: Olefin system wax which has a carboxyl group [diamond KARUNA -30 by Mitsubishi Kasei Corp., and acid-number 75 mgKOH/g]

W-2: olefin system wax [which has a carboxyl group — yes made from Mitsui Petrochemistry — wax oxidation type 2203A and acid-number 30 mgKOH/g]

W-3: The olefin system polymer which has a carboxyl group [EGUZERO VA-1803 made from Exxon Chemistry A, and the 0.65 % of the weight of the amounts of maleic anhydrides]

W-4: maleic-anhydride [— : made from Wako Pure Chem Industry — best]

W-5: olefin system wax [which does not have a carboxyl group — yes made from Mitsui Petrochemistry — wax 200P]

W-6: The olefin system polymer which does not have a carboxyl group [high ZEKKUSU powder 2100JP made from Mitsui Petrochemistry]

PCL : poly caprolactone P-1:poly caprolactone [the plaque cel H-1 by Daicel Chemical Industries, Ltd., and number average molecular weight 10,000]

P-2: Poly caprolactone [the plaque cel H-7 by Daicel Chemical Industries, Ltd., and number average molecular weight 70,000]

[0023]

[A table 1]

	樹脂 種類	導電性繊維		COL		PCL		電磁波 遮蔽効 果(dB)	衝撃強さ (kgf.cm/cm)	スパイラ ルフロー 値 (cm)	表面外 観
		種類	量 (容量%)	種類	量 (重量部)	種類	量 (重量部)				
実施例1	PC	NICF	4.7	W-1	0.5	P-1	5.0	49	11.7	17.6	○
実施例2	"	"	4.7	W-2	0.5	"	5.0	46	9.3	17.5	○
実施例3	"	"	4.7	W-1	3.0	"	5.0	72	12.5	17.8	○
実施例4	"	"	4.7	W-3	10.0	"	5.0	53	17.2	18.9	○
実施例5	"	"	10.0	W-1	0.5	"	6.5	71	11.3	16.8	○
実施例6	"	SUS	1.0	"	1.0	"	5.0	55	8.1	18.5	○
実施例7	"	CF	23.0	"	1.0	"	5.0	43	10.0	15.2	○
比較例1	"	NICF	4.7	—	—	—	—	5	6.3	11.4	○
比較例2	"	"	4.7	W-1	0.5	—	—	44	13.8	11.5	×
比較例3	"	"	10.0	—	—	P-1	5.0	55	4.5	16.7	○
比較例4	"	"	4.7	W-3	40.0	"	5.0	混	練	不	可
比較例5	"	SUS	1.0	—	—	"	5.0	4	3.9	18.3	○
比較例6	"	CF	23.0	—	—	"	5.0	26	4.6	15.1	○
比較例7	"	NICF	4.7	W-4	0.15	"	5.0	6	6.2	17.6	○
比較例8	"	"	4.7	W-5	0.5	"	5.0	6	6.4	17.7	○
比較例9	"	"	4.7	W-6	0.5	"	5.0	6	6.5	17.7	○
比較例10	"	"	4.7	W-1	0.5	"	13.0	混	練	不	可
比較例11	"	"	10.0	"	0.5	"	0.5	70	12.9	10.5	×
比較例12	"	"	10.0	"	0.5	P-2	6.5	71	11.5	18.0	△

[0024]

[A table 2]

	樹脂 種類	導電性繊維			COL		PCL		電磁波 遮蔽効 果(dB)	衝撃強さ (kgf. cm/cm)	スパイラ ルフロー 値 (cm)	表面外 観
		種類	量 (容重%)	種類	種類	量 (重量部)	種類	量 (重量部)				
実施例8	ABS	NICF	4.1	P-1	P-1	1.0		5.0	50	10.3	24.4	○
実施例9	PBT	"	5.1	"	"	1.0		5.0	48	10.0	27.8	○
比較例13	ABS	"	4.1	-	-	-		-	8	5.3	18.9	△
比較例14	PBT	"	5.1	-	-	-		-	4	3.9	22.5	○

[0025]

[Effect of the Invention] The constituent of this invention has the outstanding electromagnetic wave shielding effect, and is excellent in the shaping fluidity, the surface appearance, and the mechanical strength, and is suitable in the broad industrial field which needs the electromagnetic wave electric shielding including the case of electronic equipment, and the industrial effectiveness which does so is exceptional.

[Translation done.]